

Field Induced Transition from Metal to Insulator in the CMR Manganites

Y. Endoh, H. Nojiri[†], K. Kaneko[†], K. Hirota, T. Fukuda[‡], H. Kimura,
Y. Murakami* S. Ishihara[†], S. Maekawa[†], S. Okamoto[†] and M. Motokawa[†]

CREST, Department of Physics, Tohoku University, Sendai, 980-8578 Japan

[†] *CREST, Institute for Materials Research, Tohoku University, Sendai, 980-8577 Japan*

[‡] *SPring-8, JAERI, 1503 - 1 Kanaji, Kamigori-cho, Ako-gun, Hyogo 678-1200, Japan*

* *CREST, Photon Factory, Institute of Materials Structure Science, KEK, Tsukuba 305-0801, Japan*

(October 11, 1998)

Abstract

The gigantic reduction of the electric resistivity under the applied magnetic field, CMR effect, is now widely accepted to appear in the vicinity of the insulator to metal transition of the perovskite manganites. Recently, we have discovered the first order transition from ferromagnetic metal to insulator in $\text{La}_{0.88}\text{Sr}_{0.12}\text{MnO}_3$ of the CMR manganite. This phase transition induces the tremendous increase of the resistivity under the external magnetic field just near above the phase transition temperature. We report here fairly detailed results from the systematic experiments including neutron and synchrotron X-ray scattering studies.

keywords: Metal Insulator Transition, CMR Manganites, Orbital Order, Charge Order, Superexchange, Anisotropic Tensor Susceptibility, Neutron scattering, Synchrotron x-ray scattering

I. INTRODUCTION

The Metal - Insulator (MI) transition accompanied with the colossal magneto- resistance (CMR) effect in the manganese oxides (manganites) has been elucidated along the concept established in the studies for the strongly correlated electron systems [1]. Namely, LaMnO_3 of the parent material of CMR is recognized as the Mott Insulator (Charge Transfer type like La_2CuO_4). The "double exchange" interaction in these doped manganites was first proposed in 1950s [2], but the presently discussed CMR effect cannot be comprehensive solely within this simple context of the "double exchange" mechanism [3]. Furthermore, unusual properties of the CMR effect are regarded as cooperative phenomena associated with the structural change due to a tiny atomic displacement, competing magnetic interactions and charge fluctuations between different valencies of manganese cations.

In this respect, Mn^{3+} orbitals in LaMnO_3 are Jahn-Teller (*JT*) active [4], hence the degenerated e_g "orbital" of *d*-electrons in the cubic crystalline field can be easily lifted by lowering the crystal symmetry costing the lattice distortion energies. In fact, LaMnO_3 is the antiferromagnetic insulator with the orthorhombic lattice structure (space group *Pnma*). Then the doping of holes by substituting trivalent La to divalent Sr cations promotes the simultaneous change in both magnetism and conductivity, which has been recognized to be originated by the "double exchange" mechanism [2]. Since the CMR effect cannot be compatible to this simple mechanism, it has been believed that the CMR should result from the effect of the local distortion which is often defined as "polarons" [5]. The itinerancy of such polarons give rise to the conduction by either applying the magnetic field or decreasing temperature. However, there has been no definitive experimental result showing the existence of the polarons except speculative interpretation of data of electrical conductivity, mainly. Nonetheless, it is well recognized that the *JT* interaction plays a crucial role to determine the superexchange interactions in these transition metal oxides.

In this presentation, we focus on very unusual bulk properties in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x \approx 0.12$) associated with not only the charge order (CO) but the "orbital" order (OO) and

discuss that the CMR effect can be comprehensive by the role of the "orbital" degree of the freedom [6]. In order to investigate this subject in detail, we have conducted a decisive observation of the OO in the typical CMR manganites. Since this method is not familiar but very novel, we therefore briefly describe the principle of the experimental method [7]. Then we will argue that the electron correlations also act a significant key role for the OO and eventually the CMR effect is relevant to the phase transition in the manganites.

The format of the paper is as follows. Bulk properties, in particular associated with the phase transition from ferromagnetic metal to insulator in the $\text{La}_{0.88}\text{Sr}_{0.12}\text{MnO}_3$ by either lowering temperature and applying the external field are presented. The experimental results of the OO will be followed by the description of the principle of detection of OO. Then the final section is devoted to discussions of our recent experimental results based on the recent novel concept of the "phase separation".

II. BULK PROPERTIES OF $\text{LA}_{0.88}\text{SR}_{0.12}\text{MNO}_3$

$\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ is recognized to be simplest among many CMR manganites and also it is the most extensively investigated material so far. Even so, the phase diagram of this system is already complicated near $x \approx 0.1$, where several phase boundaries of insulator-metal, lattice symmetry as well as magnetic structure are entangled with each other on the temperature (T) - doping concentration (x) diagram as shown in Fig. 1 [8]. In other words, if we understand correctly this complexity in the phase diagram, we might find a possible clue to the CMR mechanism in the manganites.

The CO, lattice distortion and magnetic properties presumably couple with each other around $x \approx 0.125$ (1/8), but we must make it sure what extent and how. In order to elucidate this particular subject, it is important to grow a high quality single crystal. Now we all know that high quality single crystals can be grown by the conventional floating zone method using a lamp image focusing furnace. After characterizing this single crystal, which is determined to be $x = 0.12$, we have systematically investigated both bulk and microscopic

characters [9]. Here, we summarize the essence of our experiments showing an unusual phase transition from ferromagnetic metal to insulator transition by either applying magnetic field or reducing temperature [10].

First, we confirmed that sequential structural phase transitions occur varying temperature as shown in Fig. 2. Upon cooling from high temperatures, the crystal symmetry undergoes from pseudo-cubic to orthorhombic at $T_H = 291K$. Then ferromagnetic long range order (lro) occurs below $T_C = 170K$ in the orthorhombic phase. The crystal symmetry changes again from orthorhombic to another pseudo cubic at $T_L = 145K$ accompanied with the jump in magnetic structure, which seems to be reentrant to the pseudo-cubic structure [8], but in fact it is not so simple as described below.

According to high-resolution synchrotron x-ray powder diffraction at NSLS in BNL, the determined crystal structure is more complicated [11]. The powder sample for this particular experiment was prepared by carefully crushing a small piece of the single crystal under acetone and was highly crystalline, with peak width of $\approx 0.01^\circ$, close to the instrumental resolution. The crystal structure above T_H is not pseudo cubic but in fact orthorhombic (*Pnma*). Moreover, a splitting of some of the diffraction peaks was seen below 350K, which was confirmed to be a single phase at 400 K. Then both phases underwent reentrant-type transitions as just described above, the majority phase at 295K and 145K, and the minority phase (20%) at 320 K and 120 K, with $b/\sqrt{2} < a \approx c$ in the intermediate temperature region, characteristic of the *JT* ordered state. 20% of the minority phase was assigned to be the phase of relatively dilute Sr or hole concentration. The phase transition at T_H is characterized by the abrupt decrease in the b lattice parameter indicating the onset of the *JT* orbital ordering of LaMnO₃ type. Then the crystal structure below T_L was not well determined due to the considerable lowering of the symmetry, presumably triclinic (*P2*). Note that the symmetry of the intermediate mixed phase is not orthorhombic but monoclinic ($\gamma \approx 90.1^\circ$). Though a further refinement is necessary, we have obtained rather important evidence of both phase separation and the change of the different crystal symmetry at above T_H and below T_L from this precise structural determination.

Next, we summarize here the results of bulk measurements, in particular the magnetic properties under the external magnetic field [10]. Most of such experiments were performed at the high magnetic field laboratory of IMR, Tohoku university. We confirmed following important evidence of the excellent $\text{La}_{0.88}\text{Sr}_{0.12}\text{MnO}_3$ single crystal from systematic magnetization measurements. The magnetization process shows a fairly weak anisotropy. This fact indicates that even below T_L , the canting of magnetic moment observed by neutron diffraction is not due to the major part of the single ion anisotropy, but presumably due to a weak anisotropic interaction by the lowering the crystal symmetry. Then there appears a hysteresis loop showing a jump in the magnetization process at each temperature between T_L and T_C in the intermediate phase. The transition field depends upon temperature, which increases monotonically with temperature. The hysteresis loop was confirmed to appear in both the megnetoresistance and magnetostriction measurements simultaneously. From the magnetoresistance measurements as shown in Fig. 3, we discovered very astonishing experimental evidence that the resistance abruptly increases at the transition field, which indicates the transition from metal to insulator at external fields in a certain temperature range of $T_L < T < T_C$. As already described above, the transition temperature increases as the increase of the magnetic field. Since the transition is associated with a clear jump in the magnetostriction, the metal-insulator phase transition is accompanied with the lattice distortion. Then the kinematical effect of the transition, or the relaxation effect in the magnetization in the field can well be interpreted by this fact accompanying the lattice distortion or the large magntostriction effect.

According to the detailed analysis of the magnetization data, the jump at the transition field in magnetization is not due to the increase of the spontaneous magnetic moment, but due to the difference of the Curie temperature. In other words, the asymptotic Curie temperature of the lower temperature phase is higher than the actual T_C (225 K). Then there appears another clear jump in magnetic susceptibility, χ at T_H , indicating the asymptotic Weiss temperature, where the $\chi^{-1} - T$ curve crosses zero, is about 205K for the higher temperature phase. It means that the magnetic interaction does change in each phase with

different crystal symmetry suggesting that the interatomic interaction either superexchange or "double" exchange interaction is very sensitive to the atomic configuration.

The latest measurements of the x dependence of the magnetic properties around $x \approx 0.12$ show that the transitions in this range are very sensitive to x . Even changing 1% level in x (11 – 12.5%), the transition behavior changes significantly, which may reflect the change in the lattice structure in detail, though qualitatively no significant difference was reported so far.

Now let's describe the results of neutron diffraction measurements. Above $T_L = 145K$, only $(2,0,0)$ ferromagnetic component appears, which indicates a simple 3 dimensional (3D) isotropic ferromagnetic order below $T_C = 170K$. Below $T_L = 145K$, the very weak but distinct signal appears at $(0,0,1)$ indicating that a tiny antiferromagnetically ordered component appears perpendicular to the $(1,0,0)$ plane. Since the magnetization curves show no difference in crystal orientation, the net magnetic moment simply inclines from the C axis by few degrees, probably $3 - 4^\circ$, so that the magnetic state is precisely the canted antiferromagnet, but the nature is ferromagnetic in principle. Then it is reasonable that the spin wave dispersion of $x = 0.12$ crystal is fairly isotropic with almost zero energy gap at the zone center [12]. The conductivity is apparently isotropic reflecting the isotropic ferromagnetic nature determined both bulk magnetic properties and spin dynamics, which is significant contrast to the character of LaMnO_3 [13].

The most fascinating feature is that the resistivity jumps in enhanced manners under the applied field slightly above T_L as shown in Fig. 3. It means that in this temperature range, $T_L < T < T_C$, there appears a striking phenomenon of the strong positive magneto-resistance effect in the CMR manganese oxides. Furthermore, the crystal undergoes the transition to a less distorted phase below T_L , accompanied with the metal-insulator transition behavior. It is highly possible, therefore, that the CO is established below T_L . Then we searched for the forbidden Bragg reflection of $(2,0,1/2)$ below T_L with a positive answer. Note that forbidden reflections of $(h, k, l + 1/2)$ with integer h, k, l are specified to the superlattice reflections due to the CO, which indicates that Mn^{4+} cations localize at the center surrounded 8 Mn^{3+}

units in every other C layers [14]. The transition is definitely of the first order with distinct thermal hysteresis as well as the abrupt jump in intensity at T_L . In order to confirm that this phase transition in the magnetic field is continued from the zero field, we performed the scans around both the fundamental Bragg reflection of (4,0,0) and the superlattice reflection of (2,0,1/2) changing the external magnetic field at several fixed temperatures between T_L and T_C . Then we really observed that both structural transition and CO occur at the transition field assigned by the bulk measurements. Thus all the results concerning the phase transition are consistent with every respect.

III. DETECTION OF ORBITAL ORDERING BY SYNCHROTRON X-RAY SCATTERING

We now speculate that the drastic change in both magnetic properties and conductivity accompanied by the crystal distortion as described in the preceding section might be controlled by a "hidden" parameter of the "orbital" degree of freedom. The most decisive way to investigate the OO at this moment is applying the novel method of the synchrotron x-ray scattering technique established quite recently.

By tuning the synchrotron radiation energies at the resonant transition energy between 1s core and 4p unoccupied electronic level corresponding to the energy of Mn K edge we could observe the orbital ordering structure, which was first demonstrated for the CO and OO in the single layered $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ where Mn^{3+} and Mn^{4+} are mixed equally ($x = 0.5$) by Murakami et al. [7]. Then the result of the OO driven by the JT interaction in LaMnO_3 was also reported quite recently [15]. Here we briefly describe the principle of this method of the detection of the OO.

The most important character of the synchrotron radiation source is not only the brightness of the coherent x-ray beam but the energy tunability by continuous scans of the monochromator. The polarization dependence of the anomalous scattering factor arises in the anisotropy of the charge, which may be determined either as the bond or orbital,

which was first pointed out by V.E.Dmitrienko [16]. He defined the scattering of anomalous tensor of charge susceptibility (ATS scattering), since the anomalous scattering amplitudes of $\Delta f'(E)$ and $\Delta f''(E)$ are written as the tensor, not the scalar for the normal charge scattering. Such a polarization dependent photo-absorption is readily known as the dichroism or the birefringence, in electromagnetic forces which rotates the polarization of the light. The essence of the polarization dependent phenomenon is the same as that of the anisotropy of the charge susceptibility caused through the resonant scattering, which is enhanced near the absorption edge. The ATS scattering enhanced at the energies near the K edge usually appears at the reflection forbidden by the atomic configuration of the crystal. Taking $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$, for instance, in addition to a class of the forbidden $(h, k, 0)$ reflections with h, k of the half integer for the CO, the $(3/4, 3/4, 0)$ is also the forbidden reflection which is only allowed by the OO of $(3z^2 - r^2)$ type in e_g band of Mn^{3+} . The ATS scattering due to the OO was clearly shown by the careful experiments; energy scans, polarization dependence (σ to π), (σ to σ) or (π to π), the special scan with rotating the crystal around the scattering vector (azimuthal scan) and so forth. Polarization switching as well as the angle dependence in the azimuthal scan are only characterized for the ATS scattering. In other words, the amplitude of ATS scattering becomes a tensor rather than a scalar reflecting the anisotropy of the orbitals.

Then the ATS scattering phenomenologically derived by Dmitrienko was clarified by taking the detailed mechanism of the polarization dependent synchrotron x-ray scattering into theoretical consideration [17]. The resonant elastic scattering near the K absorption edge is due to the elastic dipole transition. In other words, the synchrotron light excites electrons from $1s$ to $4p$ and then the resonant light is emitted resonating with the loss process of excited electrons. The formulation of the resonant x-ray scattering process [18] was extended to the present case of the anomalous process of the dipole transition. The anomalous scattering factor of $\Delta f'(E)$ and $\Delta f''(E)$ is written in the following formula, where the electronic system is excited from the initial state, $|0\rangle$ with energy ε_0 to the intermediate state, $|l\rangle$ with ε_l , and is finally relaxed to the final state, $|f\rangle$ with ε_f ,

$$\Delta f_{\alpha\beta} \propto \frac{e^2}{mc^2} \sum_l \left\{ \frac{\langle f | j_{i\alpha}(-k') | l \rangle \langle l | j_{i\beta}(k'') | 0 \rangle}{\varepsilon_0 - \varepsilon_l - \omega_{k''} - i\delta} + \frac{\langle f | j_{i\alpha}(k'') | l \rangle \langle l | j_{i\beta}(-k') | 0 \rangle}{\varepsilon_0 - \varepsilon_l + \omega_{k''} - i\delta} \right\}, \quad (1)$$

$$j_{i\alpha} = \frac{eA_\alpha(\vec{k})}{m} \sum_\sigma P_{i\alpha\sigma}^\dagger s_{i\sigma}, \quad (2)$$

α, β : polarization of photons (3)

$\omega_{k'(k'')}$: incident (scattered) photon energy with momentum $k'(k'')$

δ : constant

$A_\alpha(\vec{k})$: coupling constant ($4p$ (operator $P_{i\alpha\sigma}^\dagger$) $\rightarrow 1s(s_{i\sigma})$) .

Here the real and imaginary parts of $\Delta f_{\alpha\beta}$ are respectively $\Delta f'(E)$ and $\Delta f''(E)$. Regarding to this formula, the dichroism or birefringence of the light occurs by the same type of microscopic elastic dipole transition. Then a question arises why the ATS scattering occurs due to the $3d$ orbital order, or how the $3d$ orbital ordering reflects the anomalous scattering through $1s - 4p$ transition process. According to the detailed electronic structure of the MnO_6 cluster, it was found that the $4p$ levels above the Fermi level lift the degeneracy mainly by the strong Coulomb interaction between $3d$ and $4p$ electrons in the same Mn cation, which should be defined the intra-atomic Coulomb interaction [17]. The p_z orbital lifts from both p_x and p_y , when e_g orbitals are polarized in the basal plane. In fact, the calculation showed that the energy difference of the split $4p$ levels due to the intra-atomic Coulomb interaction is $1.2 \pm 0.6\text{eV}$, which is enough to induce the anomalous scattering in the resonant process. Then the scattering tensor can be calculated by assuming the $3d$ orbital ordering. The intensity of the forbidden interaction is also given in the following formula.

$$f = \begin{pmatrix} \Delta f_{xx} & 0 & 0 \\ 0 & \Delta f_{yy} & 0 \\ 0 & 0 & \Delta f_{zz} \end{pmatrix} \quad (4)$$

$$I \propto |\Delta f_{xx} - \Delta f_{zz}|^2 \quad (5)$$

The $\Delta f''_{xx(zz)}$ for either occupied $d_{3z^2-r^2}$ or $d_{x^2-y^2}$ is the basis of the experimental observation of ATS scattering, which is the exactly same formulae as given phenomenologically. Hence, the anisotropy of the d orbital reflects the tensor form in eq.(4) as well as the azimuthal angle dependence of the ATS scattering.

So far, all the experimental results from the manganites revealed the appearance of the antiferro-type of the $d_{3z^2-r^2}$ OO where the z axis of polarization alternately directs in the C plane as predicted.

Now, we understand completely the microscopic mechanism of the ATS scattering and recognize that this method gives a decisive experimental probe to investigate the OO, hopefully the orbital fluctuations by the inelastic scattering in near future.

We anticipated the OO by the insight from various experimental evidences described in the preceding section and looked for the Bragg peak originated by the OO in the $\text{La}_{0.88}\text{Sr}_{0.12}\text{MnO}_3$ single crystal. In fact, a distinct peak appears at $(0,3,0)$ forbidden reflection below T_L [9]. In addition of thermal scans, we have continued energy scans, azimuthal angle as well as polarization dependencies. All of the results show consistently that the 3D OO appears below T_L as depicted in Fig.4. We emphasize here that the OO of the Mn^{3+} cation sites presented here occurs in the undistorted crystal of the pseudo cubic symmetry, in fact, the triclinic ($P\bar{2}$) symmetry according to the detailed powder x-ray diffraction measurement, whereas the previously observed or predicted OO arises in the JT distorted lattice. Judging from an important fact of the isotropic 3D ferromagnetic nature, the antiferro-type OO may not be the same pattern that of LaMnO_3 , but may be a unique orbital state of the hybridized orbitals of $d_{z^2-x^2(y^2-z^2)}$ and $d_{3x^2-r^2(3y^2-r^2)}$, predicted by the recent theories [19].

Now, we interpret this experimental fact in terms of the recent theoretical result based on the model Hamiltonian where both spin and orbital degrees of freedom are treated on an equal footing. The phase diagram is derived at $T = 0$ with varying the exchange parameter of superexchange interaction of t_{2g} band. This mean field calculation suggests that two kinds of ferromagnetic phase exist at the different carrier concentration, namely $x < 0.08$ and $x > 0.42$ [19]. Then these two ferromagnetic phases are associated with two different orbital

structures and there exists a phase separated region between 2 phases in $0.08 < x < 0.42$. This model calculation contains the common aspects with experimental evidence showing that the stabilization of the ferromagnetic insulator phase by both applying magnetic field and reducing temperature for the $x = 0.12$ crystal : (1) both ferromagnetic ordering and antiferro-type orbital ordering are cooperatively stabilized in 3D manners, (2) the magnetic moment is apparently enlarged at the transition by changing dominant magnetic coupling from double exchange to superexchange interaction. Then more importantly, this concept of the microscopic phase separation or the phase mixture for the intermediate range, $T_L < T < T_C$, can be extended to the CMR effect occurring for $x > 0.25$ near below T_C , where the transition from the mixed phase with disordered orbitals which behaves like paramagnetic insulator to the ferromagnetic metal.

IV. DISCUSSIONS AND CONCLUDING REMARKS

As described above, one of the essential results is the direct evidence of the OO in $\text{La}_{0.88}\text{Sr}_{0.12}\text{MnO}_3$ single crystal with the same azimuthal angle dependence as that of the undoped LaMnO_3 . However it should be emphasized here the fact that the intensity appears only below T_L , where the notable JT distortion does not exist. Thus the antiferro-type OO is not the one associated with the JT lattice distortion. At the same time, the spin-wave dispersion relation as well as the electrical resistivity, magnetization in $\text{La}_{0.88}\text{Sr}_{0.12}\text{MnO}_3$ are of all isotropic nature, which is fairly in contrast to that of undoped LaMnO_3 of 2D ferromagnetic character. Therefore, the orbital state in this crystal should be different from the ordering of $d_{3x^2-r^2}/d_{3y^2-r^2}$ in LaMnO_3 . The theoretically predicted OO is the hybridized orbitals as described in the preceding section.

Next, the intermediated state was found to be phase separated according to the precise structure refinement, though the phase separation does not start to coordinate with the phase transition at T_H but grows around 305K. Since we could not observe both the OO and CO in the intermediate phase, though the scans were limited, we conjecture that the

intermediate phase would not be uniform in many respects. We must consider more in the future experiments how the phase segregated structure in the intermediate temperatures can be relevant to the microscopically mixed phase as theory predicts. Since it is very essential to consider the inherent relation with the CMR effect, we leave this conclusion to the future investigations.

As for the last point in the present paper, we propose a new concept of the anomalous phenomena appeared near the Mott transition, which should be common in the doped Mott insulator such as the high temperature superconducting copper oxides. It would contain a novel notion of the microscopic "phase separation" [20]. In the simple mean field view, the transition from insulator to metal, or Mott transition is considered to occur crossing the so called "critical" point, often called the "quantum critical" point for the doped cuprates. However, we don't think that the nature may be so simple. Furthermore the doped carriers cannot be uniformly distributed in the lattice space, in particular for the semi diluted concentration range of doped carriers. In this respect, the doped carriers might order at the special concentration such as 1/8 of the average uniform concentration of charges, which is very close to $\text{La}_{0.88}\text{Sr}_{0.12}\text{MnO}_3$. It also contains the new notion that the OO and CO is the result of the strong electron correlations, not driven by the *JT* distortion so far considered. Though we need further experimental investigations, we observed for the first time that the metallic state in the intermediate phase shows the first order phase transition to the insulator by further cooling or applying the external magnetic field. Extending this scenario to the carrier rich concentration of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ where x is around the CMR effect occurred, one might expect another phase transition from the mixed phase of the paramagnetic state showing the poor conductivity to the ferromagnetic phase with good conductive state by reducing the entropy either applying the magnetic field or cooling, which is defined the genuine CMR effect. Finally we would like to note that we do not have a concrete idea how the present model differs from the "polaron" model, but we believe that the role of the "orbital" is significant in the drastic phase transition occurred in $\text{La}_{0.88}\text{Sr}_{0.12}\text{MnO}_3$. Nevertheless the future experiments should clarify these two concepts.

Acknowledgement

Authors acknowledge dedicating assistance of A.Nishizawa and M.Onodera in the single crystal preparation of manganese oxides. They also thank Y.Tokura, G.Shirane, N.Nagaosa, D.E.Cox, M.Blume for their stimulating discussions throughout the present work. The work has partly been supported by a Grant in Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan in addition to the Core Research for Evolutional Science and Technology (CREST) by the Japan Science Technology Corporation.

REFERENCES

- [1] Y. Tokura, A. Urushibara, Y. Moritomo, T. Arima, A. Asamitsu, A. Kido and H. Furukawa, *J. Phys. Soc. Jpn.*, **63**, 3931 (1994).
- [2] C. Zener, *Phys. Rev.*, **82**, 403 (1951); P. W. Anderson and H. Hasegawa, *Phys. Rev.*, **100**, 671 (1955); P.G.de Gennes, *Phys. Rev.*, **118**, 141 (1960) .
- [3] R. M. Kusters, D. A. Singleton, D. A. Keen, R. McGreevy and W. Hayes; *Physica* **B155**, 362 (1989)
- [4] J. B. Goodenough, *Phys. Rev.*, **100**, 564 (1955); J.Kanamori, *J. appl. Phys.* **31**, 14S (1960).
- [5] A. J. Millis, P. B. Littlewood and B. I. Shraiman; *Phys. Rev. Lett.*, **74**, 5144 (1995).
- [6] S. Ishihara, M. Yamanaka and N. Nagaosa; *Phys. Rev. B* **56**, 686 (1997).
- [7] Y. Murakami, H. Kawada, H. Kawata, M. Tanaka, T. Arima, Y. Morotomo and Y. Tokura, *Phys. Rev. Lett.*, **80**, 1932 (1998).
- [8] H. Kawano, R. Kajimoto, M. Kubota and H. Yoshizawa, *Phys. Rev. B* **53**, R14712 (1996).
- [9] Y. Endoh, K. Hirota, Y. Murakami, T. Fukuda, H. Kimura, H. Nojiri, K. Kaneko, S. Ishihara, S. Okamoto and S. Maekawa; unpublished.
- [10] H. Nojiri, K. Kaneko, M. Motokawa, K. Hirota and Y. Endoh; unpublished.
- [11] D. E. Cox, T. Iglesias, G. Shirane, K. Hirota and Y. Endoh, unpublished.
- [12] K. Hirota, H. Kaneko, A. Nishizawa, Y. Endoh, M. C. Martin and G. Shirane, *Physica B* **237-238**, 36 (1997).
- [13] K. Hirota, H. Kaneko, A. Nishizawa and Y. Endoh, *J. Phys. Soc. Jpn.*, **65**, 3736 (1996).
- [14] Y. Yamada, O. Hino, S. Nohdo, R. Kanao, T. Inami and S. Katano, *Phys. Rev. Lett.*,

77, 904 (1996).

[15] Y. Murakami, I. Koyama, M. Tanaka, H. Kawata, J. P. Hill, D. Gibbs, M. Blume, T. Arima, Y. Tokura, K. Hirota and Y. Endoh, Phys. Rev. Lett., **81**, 582 (1998).

[16] V. E. Dmitrienko, Acta Cryst., **A 39**, 29 (1983); D. H. Templeton and L. K. Templeton, Acta Cryst., **A 41**, 133 (1985).

[17] S. Ishihara and S. Maekawa, Phys. Rev. Lett., **80**, 3799 (1998).

[18] M. Blume, *Resonant Anomalous x-ray Scattering -Theory and Applications-* edited by G. Materik, C. J. Sparks and K. Fisher; Elsevier Science B.V. (1994).

[19] S. Okamoto, S. Ishihara, and S. Maekawa; unpublished.

[20] S. Yunoki et al. Phys. Rev. Lett. **80**, 686 (1998).

Figure captions

Fig.1: Magnetic and structural phase diagram for $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($0 < x < 0.3$) determined by neutron diffraction data depicted at the left hand side. PM, CAF and FM are, respectively, the symbols of paramagnetic, canted antiferromagnetic and ferromagnetic phases. O^* and O' are the phases with two different orthorhombic structure. O^* was defined to be pseudo cubic in the original literature [8].

Fig.2: Sequential phase transitions observed by neutron diffraction for $\text{La}_{0.88}\text{Sr}_{0.12}\text{MnO}_3$ single crystal. Upper panel shows lattice vector of fundamental reflections and the middle shows peak intensities. The bottom is peak intensities of the ferromagnetic Bragg reflection which starts to grow below $T_C = 170\text{K}$. The phase transition at both $T_L = 145\text{K}$ and $T_H = 291\text{ K}$ is of the first order [9].

Fig.3: Upper panel shows magnetization curves measured in pulsed magnetic fields for $\text{La}_{0.88}\text{Sr}_{0.12}\text{MnO}_3$ single crystal. The vertical origin is shifted for the convenience by $-0.4mB$ each per 5K shift. Lower panel is magneto-resistance at various temperatures around our interests [10].

Fig.4: ATS scattering from $\text{La}_{0.88}\text{Sr}_{0.12}\text{MnO}_3$ single crystal. Upper panel shows the data of energy scan. Distinct peak at $(0\ 3\ 0)$ appears at 6.552 keV, where absorption reaches maximum. The middle shows the azimuthal angle scan and the bottom shows thermal evolution of the peak intensities [9].

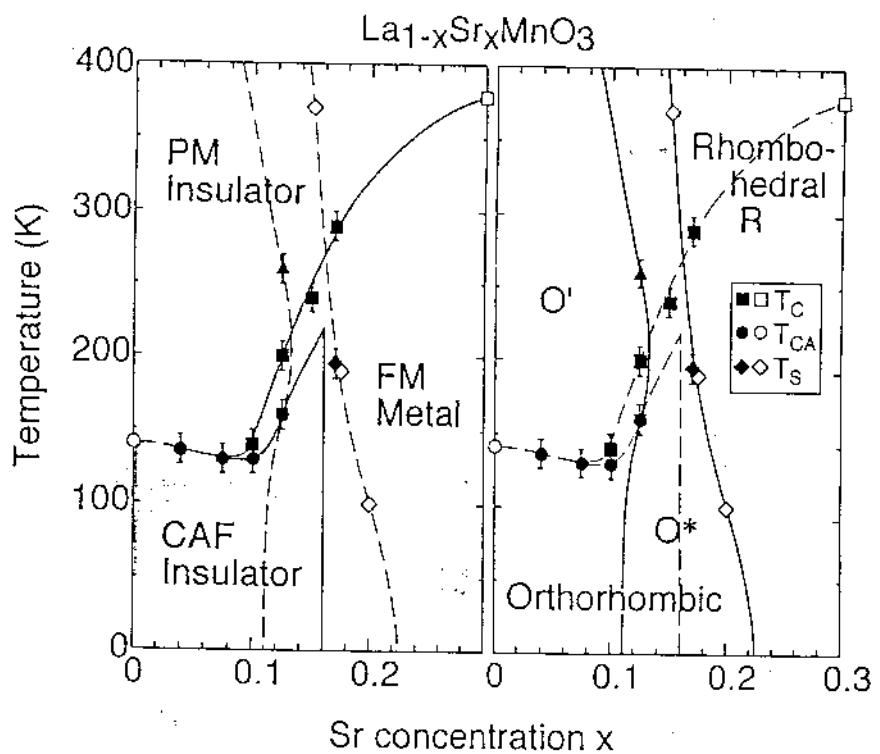
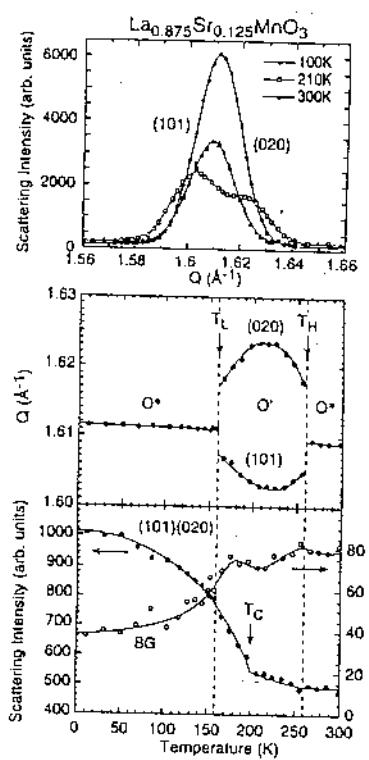


Fig. 1 Y.Endoh et al.

$\text{La}_{0.88}\text{Sr}_{0.12}\text{MnO}_3$

